IMPROVED MAGNETIC REFRIGERATORS WITH Hi-Tc SUPERCONDUCTING MAGNETS

Charles Gallo

Superconix, Inc.
261 Fifth St East
Saint Paul MN 55101

April 1993

19960215 036

Final Report

PHILLIPS LABORATORY
Space and Missiles Technology Directorate
AIR FORCE MATERIEL COMMAND
KIRTLAND AIR FORCE BASE, NM 87117-5776

UNCLASSIFIED

AD NUMBER

AD-B207 026

NEW LIMITATION CHANGE

TO

DISTRIBUTION STATEMENT A -
Approved for public release; Distri-
bution unlimited.

Limitation Code: 1

FROM

DISTRIBUTION STATEMENT -

Limitation Code:

AUTHORITY

Janet E. Mosher; Phillips Lab/CA, Kirtland AFB, N.M.

THIS PAGE IS UNCLASSIFIED

PL-TR-93-1108
This final report was prepared by Superconix, Inc., St. Paul MN Contract F29601-93-C-0112
Job Order, 9991SB1R, with Phillips Laboratory, Kirtland Air Force Base, New Mexico. The
Laboratory Project Officer-in-Charge was Marko Stoyanof (VTPT).

This report has been reviewed and is approved for publication.

Marko M. Stoyanof
MARKO STOYANOF
Project Officer

                                              FOR THE COMMANDER

David H Kristensen   *Henry L Pugh*
DAVID KRISTENSEN, Lt Col, USAF   HENRY L. PUGH, JR., Col, USAF
Chief, Space Power and   Director of Space and Missiles Technology
Thermal Management Division

DRAFT SF 298

1. Report Date (dd-mm-yy) April 1993	2. Report Type Final	3. Dates covered (from... to) 11/92 to 4/93
4. Title & subtitle Improved Magnetic Refrigerators With Hi-Tc Superconducting Magnets		5a. Contract or Grant # F29601-93-C-0112
		5b. Program Element # 62601F
6. Author(s) Charles Gallo		5c. Project # 9991
		5d. Task # SB
		5e. Work Unit # 1R
7. Performing Organization Name & Address Superconix, Inc. 261 Fifth St East Saint Paul, MN 55101		8. Performing Organization Report #
9. Sponsoring/Monitoring Agency Name & Address Phillips Laboratory 3550 Aberdeen Ave SE Albuquerque, NM 87117-5776		10. Monitor Acronym
		11. Monitor Report # PL-TR-93-1108

12. Distribution/Availability Statement   Distribution authorized to DoD components only; Proprietary Information; April 1993; Other requests for this document shall be referred to AFMC/STI.

13. Supplementary Notes

14. Abstract   To produce pre-formed thick-film Hi-Tc superconducting magnets with improved critical current for magnetic refrigerators, the Hi-Tc superconducting powder was coated with a thin film of beneficial metal (s) (Ag, Pb, Nb) before fabrication. It was anticipated that the metallic bonding between the Hi-Tc superconducting grains would overcome the usual "weak-links" that limit the superconducting current. This might be particularly effective with Lead and Niobium since these low temperature superconductors have long coherence lengths. After fabrication and heat treatment, the superconducting properties of the thick-films were measured, particularly the critical current (Jc). Regarding improvements in Jc of $Bi2Sr2CaCu2Ox$ thick films, Ag-coating gave improvements of +131%. However, for $Bi1.8Pb.4Sr2Ca2Cu3Ox$ thick-films, Ag-coating decreased Jc -29%, Nb-coating decreased Jc -48%, Ag+Nb-coating decreased Jc-52%, and Pb-coating chemically deteriorated the BiPb2223 superconductor.

15. Subject Terms superconductor, thin film

Security Classification of			19. Limitation of Abstract Limited	20. # of Pages 46	21. Responsible Person (Name and Telephone #) Marko Stoyanof (505) 846-2660
16. Report Unclassified	17. Abstract Unclassified	18. This Page Unclassified			

GOVERNMENT PURPOSE LICENSE RIGHTS
(SBIR PROGRAM)

Contract Number: F29601-93-C-0112
Contractor: Superconix, Inc.
             St. Paul, MN

For a period of four (4) years after delivery and acceptance of the last deliverable item under the above contract, this technical data shall be subject to the restrictions contained in the definition of "Limited Rights" in DFARS clause at 252.227-7013. After the four-year period, the data shall be subject to the restrictions contained in the definition of "Government Purpose License Rights" in DFARS clause at 252.227-7013. The Government assumes no liability for unauthorized use or disclosure by others. This legend shall be included on any reproduction thereof and shall be honored only as long as the data continues to meet the definition on Government purpose license rights.

CONTENTS

FIGURES

TABLES

SUMMARY

The overall objective is to produce pre-formed thick-film Hi-Tc superconducting magnets with improved critical current for magnetic refrigerators. To achieve this objective, the Hi-Tc superconducting powder was coated with a thin film of beneficial metal(s) (Ag, Pb, Nb) before fabrication into pre-formed thick-film magnets. It was anticipated that the resultant metallic bonding between the Hi-Tc superconducting grains would overcome the usual "weak-links" that limit the superconducting current. This might be particularly effective with Lead and Niobium since these metals are superconducting with long coherence lengths at low temperatures. After fabrication and heat treatment, the following superconducting properties of the thick-films were measured.

    (1) Superconducting transition temperature (Tc).

    (2) Critical superconducting current (Jc).

    (3) Trapped magnetic flux.

Regarding improvements in Jc of $Bi_2Sr_2CaCu_2O_x$ thick films, Ag-coating gave improvements of ~+131%. However, for $Bi_{1.8}Pb_{.4}Sr_2Ca_2Cu_3O_x$ thick-films, Ag-coating decreased Jc ~-29%, Nb-coating decreased Jc ~-48%, Ag+Nb-coating decreased Jc ~52%, and Pb-coating chemically deteriorated the BiPb2223 superconductor. The Ag-coating undoubtedly improved the ductility and strain tolerance of the fabrication and would be useful in wire technology, but that was not the objective of this project. The improvements in Jc are too marginal for further pursuit in a Phase 2 project at this time, but further efforts with other materials is justified on an exploratory basis in future Phase 1 efforts.

INTRODUCTION/OBJECTIVES

Magnetic refrigerators are very promising for many applications due to their long-life and subdued vibration. However, the size, weight, cost and refrigeration efficiency will depend on the magnet characteristics. Conventional copper-coil electromagnets are unrealistic because of their high power consumption, large size, heavy weight and need for cooling. Thus, superconducting magnets are under consideration to alleviate these problems, particularly the power consumption. Conventional "low temperature" superconducting magnets have the disadvantage of required operation at very low temperatures which reintroduces size, weight, cost and inefficiency burdens. In principle, the new "high temperature" superconductors would be very beneficial, but there are problems with fabricating these "Hi-Tc" ceramic materials into flexible wire with high current capacity.

Our innovations yield Hi-Tc superconducting magnets by utilizing "pre-formed thick-film Hi-Tc" fabrications with high critical currents that circumvent the Hi-Tc wire problems. Our proprietary magnet fabrications can also be magnetically pumped, thus eliminating the wire problems of winding, anchoring, contact resistance and thermal gradients. Our innovations briefly follow.

(1) A novel method of fabricating encapsulated $(Bi.Pb)_2Sr_2Ca_2Cu_3O_X$ Hi-Tc superconducting thick films is shown in Figure 1 which yields HIGH Tc (110K) and reasonably HIGH Jc. This proprietary encapsulation technique circumvents the problems with Pb-escape and retrograde densification that usually adversely affects Tc and Jc in this Bi2223 superconducting material. Our previous studies also revealed that the anisotropic superconducting grains were aligned with the desireable ab-plane oriented parallel to the Ag substrate in the direction of maximum current flow.

HiTc Superconductor

Ag Foil
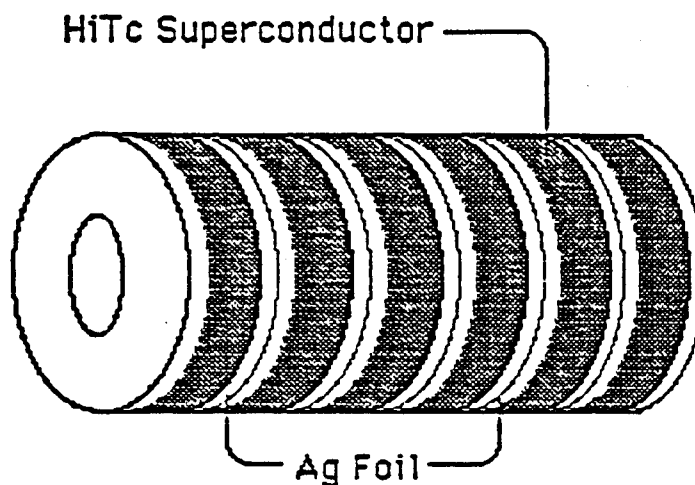
Figure 1.   Novel "sandwich" method of fabricating encapsulated
            Hi-Tc thick films and preformed magnets. For Hi-Tc
            Bi.Pb.2223 thick films, this encapsulation technique
            circumvents Pb-loss and retrograde densification and
            yields HIGH Tc (110K) and reasonably HIGH Jc with
            grain alignment. By cascading these circular annular
            thick-film sandwiches, a Hi-Tc superconducting magnet
            can be constructed as shown. These "washer-shaped"
            ring sandwiches can carry a higher total current
            because the "thickness" can be conveniently made
            larger. The superconducting current and accompanying
            magnetic field can be induced by "flux-pumping"
            schemes.

(2) The magnets can be constructed with these pre-formed Hi-Tc thick films by two different techniques, one of which is shown in Figure 1. These novel designs circumvent problems with brittle low-current Hi-Tc wires.

(3) Novel "flux-pumping" schemes can be used to magnetically induce current in the pre-formed magnets which do not require brittle wire, electrical leads or high current power supplies. A conceptual scheme is shown in our original proposal which also contains one possible configuration relevant to a magnetic refrigerator.

(4) To further improve the superconducting critical currents (Jc), the inter-granular weak-link problem may be minimized by coating the BiPb2223 superconducting particles with thin films of compatible metal(s) prior to fabrication into BiPb2223 thick films. Since the Hi-Tc superconductors are chemically complex oxide materials, the grain boundaries often contain undesireable oxides that form "weak-links" that limit the superconducting current. The metal coatings on the grains may circumvent this problem. This is particularly troublesome in the chemically difficult BiPb2223 material which decomposes irreversibly at low temperatures ~845C substantially below its effective sintering/melting temperature. Since the BiPb2223 material cannot be melt-processed or sintered to yield high density compacts with high Jc, the metal coating on the grains may serve as effective "electrical cement" at the lower sintering temperatures. THIS IS THE MAJOR TASK OF THIS CONTRACT.

(5) Further improve Jc by ion irradiation of Bi2223 superconducting particles to improve intra-granular flux-pinning, but this is beyond Phase 1 and will be attacked in the future.

(6) Use Hi-Tc superconductors as the magneto-caloric refrigeration medium with higher efficiency than the usual paramagnetic/ferromagnetic magneto-caloric refrigeration materials. This novel concept is the subject of another SDIO/Army Phase 1 SBIR contract.

The overall objective this SDIO/Air Force SBIR Contract is to produce pre-formed thick-film Hi-Tc superconducting magnets with improved critical current for magnetic refrigerators. To achieve this objective, the Hi-Tc superconducting powder was coated with a thin film of beneficial metal(s) (ex, Ag, Pb, Nb) before fabrication into pre-formed thick-film magnets. The following technical tasks were performed.

(1) Hi-Tc superconducting Bi2212 and BiPb2223 powder particles were coated with compatible metallic thin films (Pb, Ag, Nb).

(2) With the metal-coated Hi-Tc superconducting powders, encapsulated Hi-Tc thick-film magnets were fabricated.

(3) The superconducting transition temperature (Tc), critical current density (Jc) and "trapped" magnetic fields/currents of the encapsulated Hi-Tc superconducting thick films were measured.

Since the above results were NOT significantly beneficial for increasing the critical current (Jc), possible pursuit of a Phase 2 proposal and associated tasks was abandoned.

EXPERIMENTAL ARRANGEMENT

To achieve the objective of higher Jc, the first step is to coat
the Hi-Tc superconducting powder with a thin layer of beneficial
metal(s) (ex, Ag, Pb, Nb) before fabricaton into thick-film
preformed magnets. For thin-film coating the Hi-Tc powder, Figure
2 shows the sputtering equipment which was assembled and tested.
The superconducting powder particles were tumbled inside a rotat-
ing drum inside a vacuum system. Sputtering of the metal film
onto and around the surface of the superconducting particles was
achieved from a tubular metal sputtering target mounted along the
axis of the rotating drum. This system (Figure 2) proved UNSATIS-
FACTORY for several reasons with the following most critical. The
powders stuck tightly to the inner drum surface and did NOT
tumble as desired for uniform coating. The powder sticking is
probably due to triboelectric effects (especially aggravated in
vacuum). A possible solution was the introduction of a "scraper
blade" on the inside of the drum, but this approach seemed to
introduce more problems than solutions.

Thus, we switched to a different approach using a "rotating
vibrator" as shown in Figure 3. The powder is placed in a shallow
rotating/vibrating dish beneath the sputtering target. This
worked, although lumps in the Hi-Tc powder were problematic. This
technique worked better for larger size particles than the small-
er particles which had a tendency to stick together and not
vibrate/tumble as effectively.

6

VACUUM SYSTEM

ARGON
ATMOSPHERE

HiTc
POWDER
GRANULES

SPUTTERING TARGE
(CATHODE)

SILVER, LEAD, TI
OR ZINC
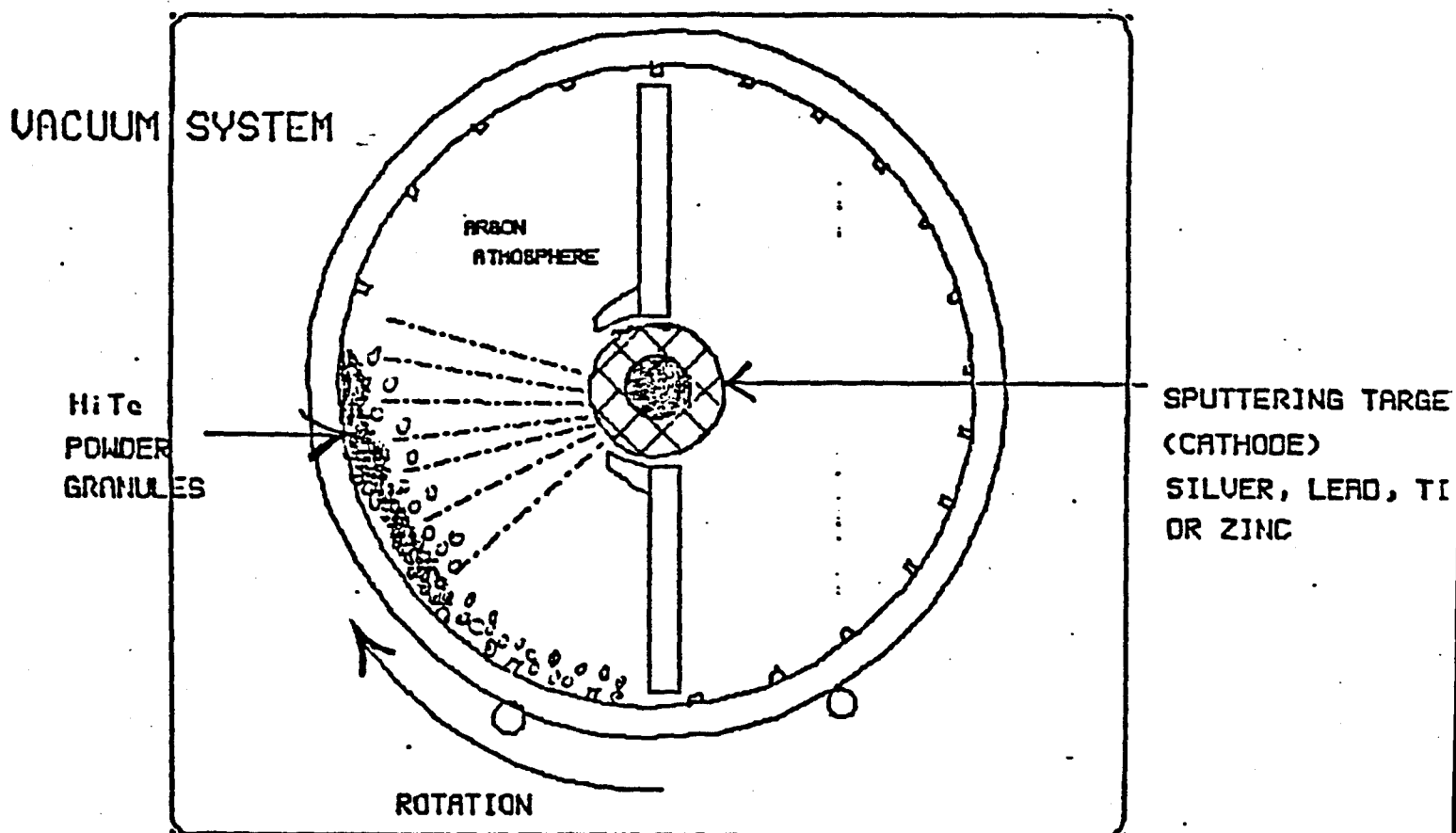
ROTATION

Figure 2.   Apparatus for coating superconducting particles with
metal films: rotating drum. The superconducting powder
particles (ex, Bi2Sr2Ca2Cu3OX) were tumbled inside a
rotating drum inside a vacuum system. Sputtering of
the metal film onto and around the surface of the
superconducting particles was achieved from a tubular
metal sputtering target mounted along the axis of the
rotating drum.

7

Vacuum

Water
Feedthru

Power
Feedthru

Cathode

Sputtering Target (Ag)

HiTc Powder

Sample Holder
(Dish)
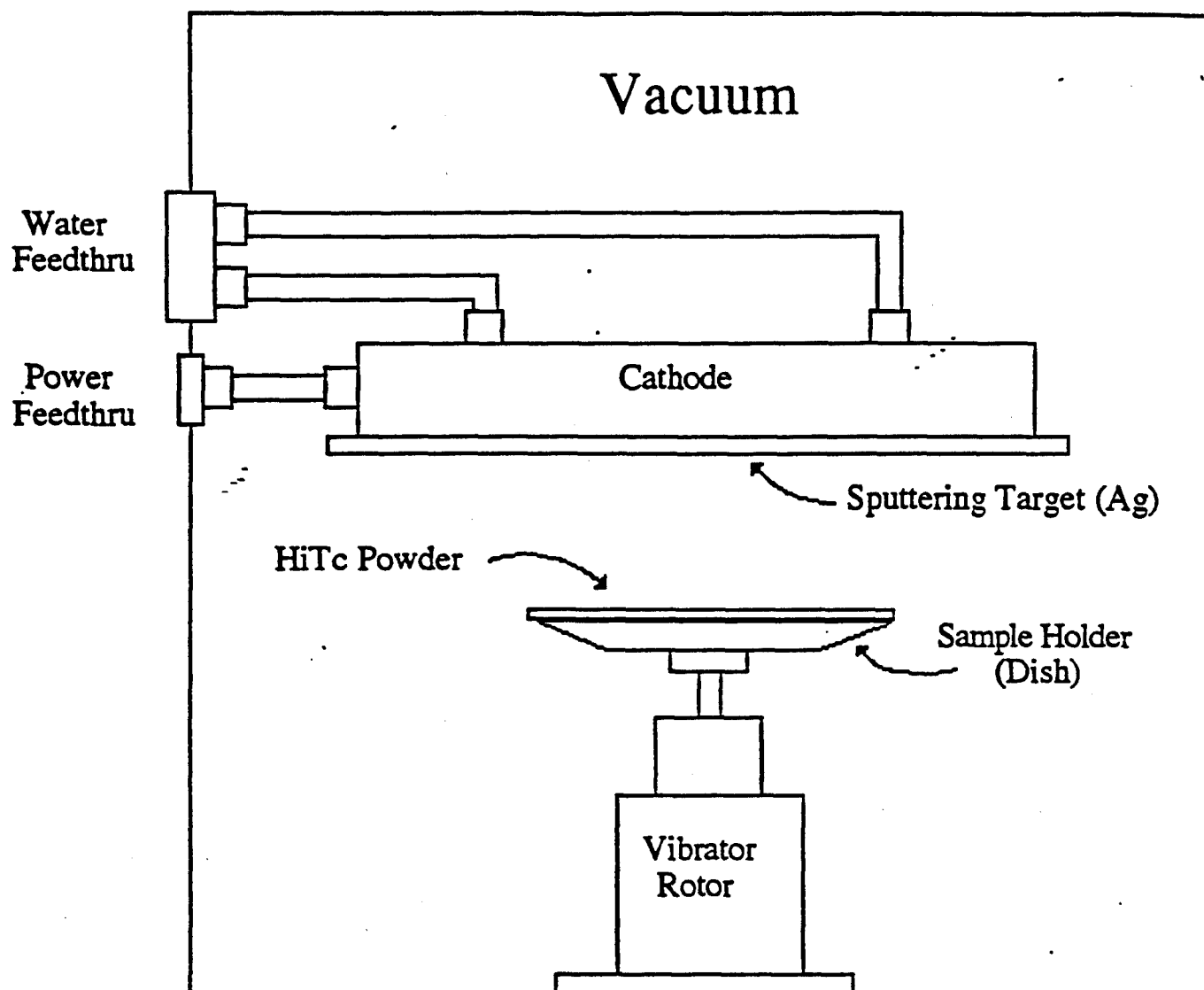
Vibrator
Rotor

Figure 3. Apparatus for coating superconducting particles with metal films: rotating/vibrating dish. The superconducting powder particles were contained in a shallow dish which was rotated and vibrated beneath a sputtering target. This produced a metallic coating around the surface of the Hi-Tc particles.

EXPERIMENTAL MEASUREMENTS/RESULTS

The Hi-Tc superconducting powders that were coated with various metals are described in Table 1 and subsequent measurements of their superconducting transition temperature Tc via magnetic susceptibility in a SQUID magnetometer in Table 2. During sputtering, a metal film was also deposited on an auxiliary substrate for monitoring the film thickness and its superconducting transition temperature Tc as described in Table 3.

After metal-coating of the Hi-Tc powder, thick-film Ag-foil sanwiches (thick-film pre-formed magnets) were pressed and sintered at various time/temperatures in various anneal gases as described in Table 4. Table 5 describes measurements of the superconducting properties as follows.

(1) Superconducting Transition Temperature (Tc). This was measured via the magnetic susceptibility on a dc SQUID magnetometer.

(2) Critical Superconducting Current (Jc). Again with the SQUID magnetometer, the magnetic hysteresis loop [magnetization (M) vs applied magnetic field (H)] was measured at constant temperature. The critical current density (Jc) was then calculated from the Bean model via

$$Jc = 20 \ dM \ / \ a(1-a/3b) \hspace{3cm} (1)$$

where dM is the width of the magnetic hysteresis loop, and a & b are the lateral sample dimensions.

(3) Trapped Magnetic Flux. This was measured on the thick-film sandwich magnets in the SQUID magnetometer as follows. First the sample temperature was raised above Tc, and then a steady magnetic field (H) was applied as the temperature was decreased below Tc to the desired steady temperature. Then, at constant temperature, the magnetic field is turned off and the magnetic moment ("trapped flux") of the superconductor (due to the per-

9

sistent superconducting current) was measured as a function of time. As expected, the persistent superconducting current was maintained with time as desired for "flux-pumping" the magnets without use of an injected current. This procedure was repeated for different magnetic fields to obtain a graph of the "trapped flux" vs applied magnetic field. This graph defines the useful magnetic range over which the superconductor may be used in the "flux-pumping trapped-flux" mode. This procedure was repeated at various temperatures to determine the useful temperature/magnetic range over which the superconductor may be used in the "flux-pumping trapped-flux" mode.

The great multitude of samples and measurements are succinctly described in Tables 1-5. In the remainder of this section, we will concentrate ONLY on those CONCLUSIVE results that have GENERIC significance.

Ag-COATED Bi2212 Hi-Tc SUPERCONDUCTORS

The most interesting data for Ag-coated Bi2Sr2CaCu2Ox thick-films is shown in Figures 4-8. The magnetic susceptibility curve (Fig 4) indicates an encouraging Tc=90K. Figure 5 shows the magnetic hysteresis loop at 10K from which the critical current density (Jc) (Fig 6) was calculated from the Bean model (Eq 1). It can be seen that an improvement in Jc~+131% was achieved with Ag-coating. As desired, the trapped flux showed a very slow time decay under all conditions and the data is shown in Figure 7 for 10K and 1,000G. In Figure 8, the trapped flux vs applied magnetic field peaked at 1,000G which indicates that this sample magnet would not be useful in flux-pumped magnetic fields above 1,000G.

10

Susceptibility vs Temperature
Ag-coated Bi2212 (H=20G) sample 7/2/93A
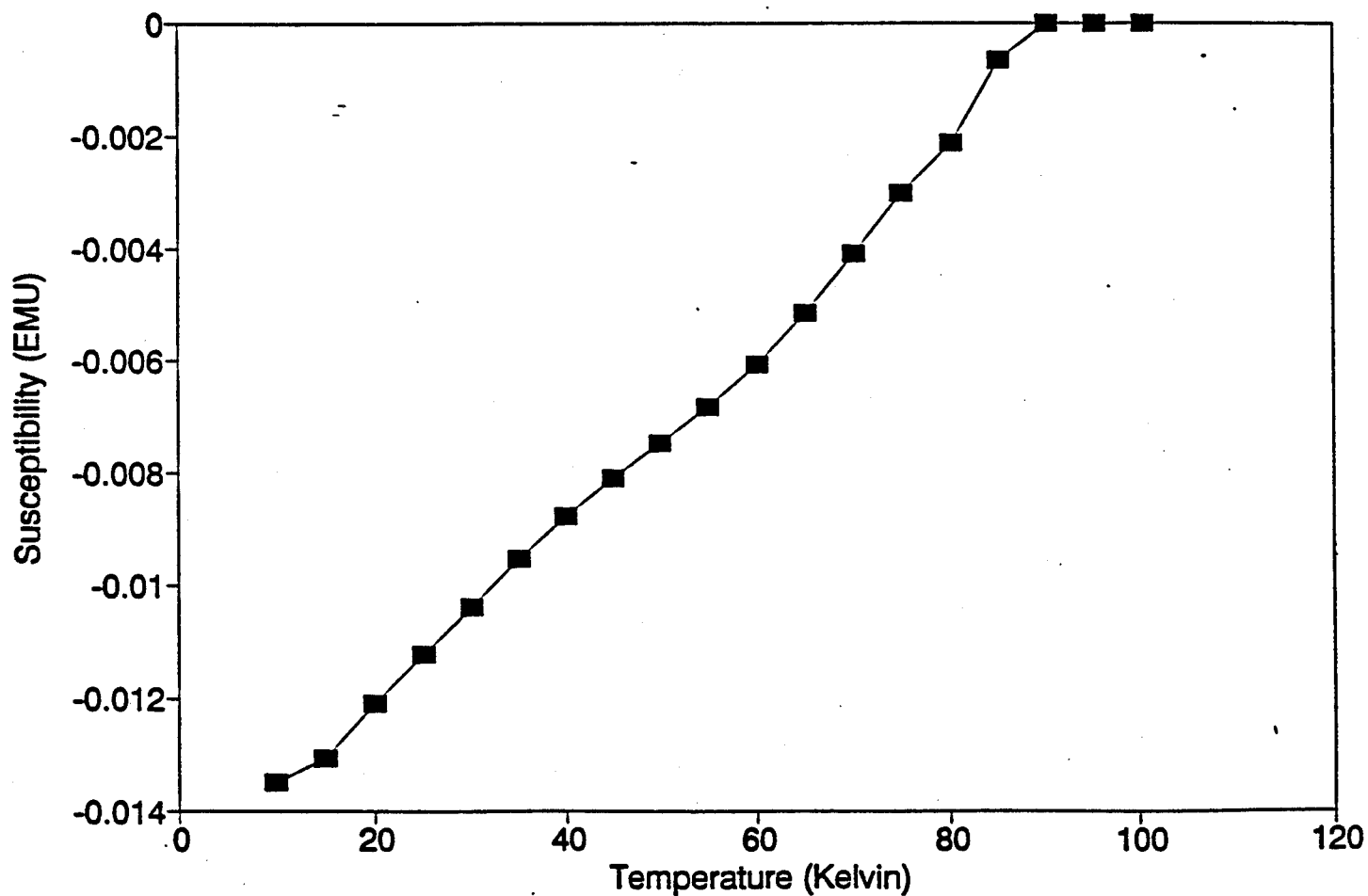
Figure 4. Magnetic susceptibility vs temperature for Ag-coated Bi2212 thick-film Ag-foil sandwich. Sample 7/2/93A.

Magnetization vs Applied Field
Ag coated Bi2212, sample 7/2/93A
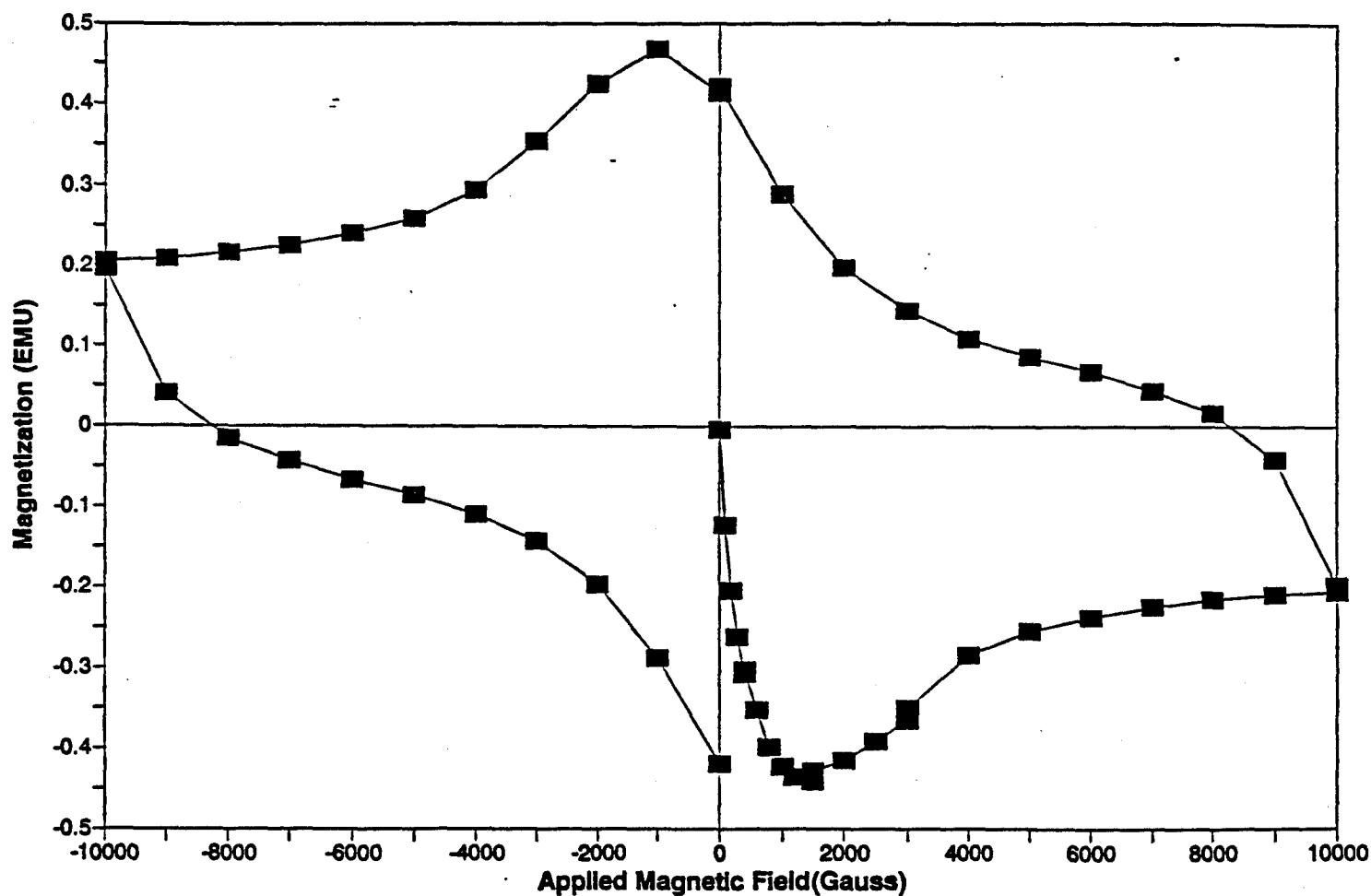
Figure 5.   Magnetic hysteresis loop for Ag-coated Bi2212
             Thick-film Ag-foil sandwich. Sample 7/2/93A. T=10K.

Jc vs H
Bi2212 (T=10K)
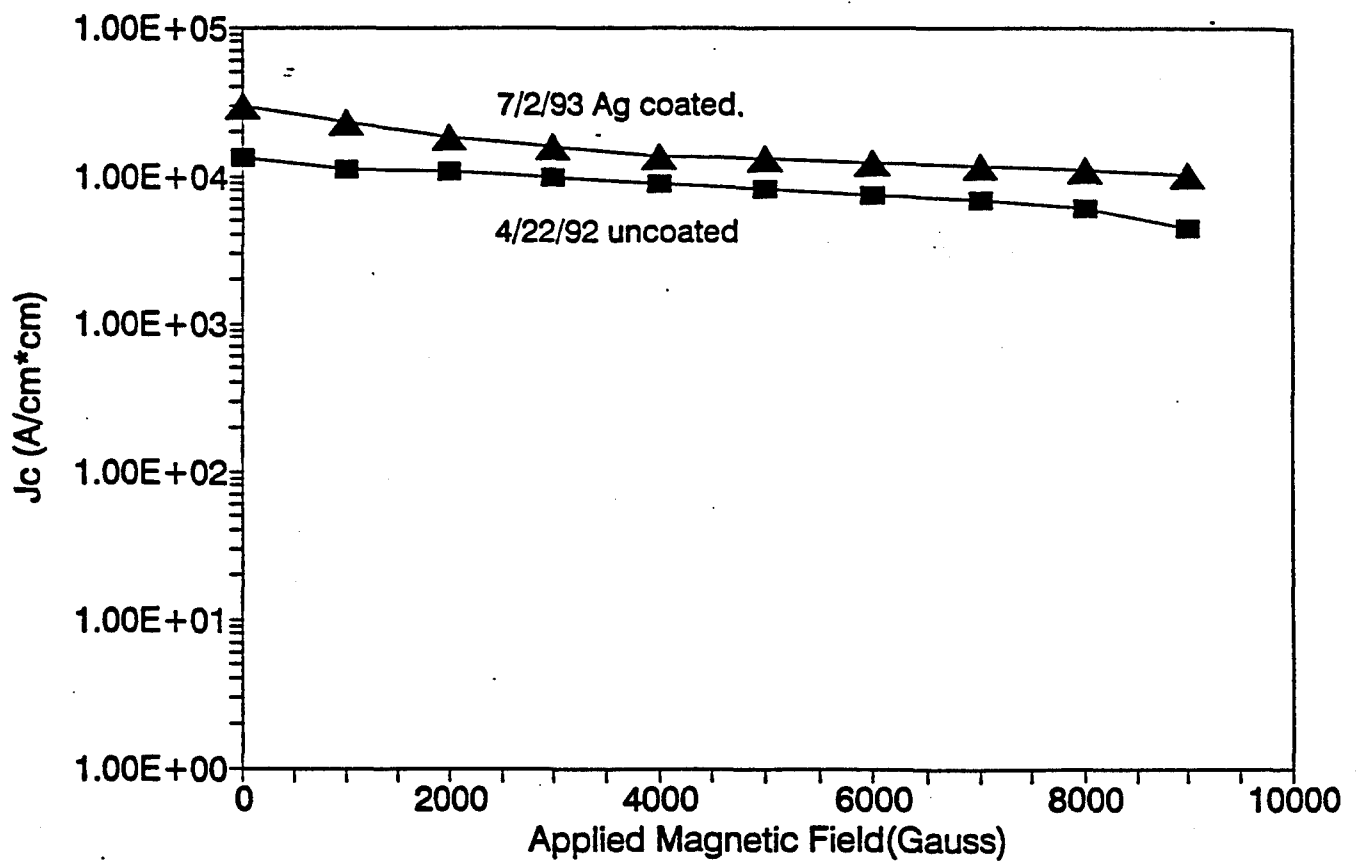
Figure 6. Critical current density (Jc) vs magnetic field for uncoated and Ag-coated Bi2212 thick-film Ag-foil sandwich. Uncoated sample 4/22/92. Ag-coated sample 7/2/93A. T=10K.

Trapped Flux vs Time
Ag-coated Bi2212 sample 7/2/93A
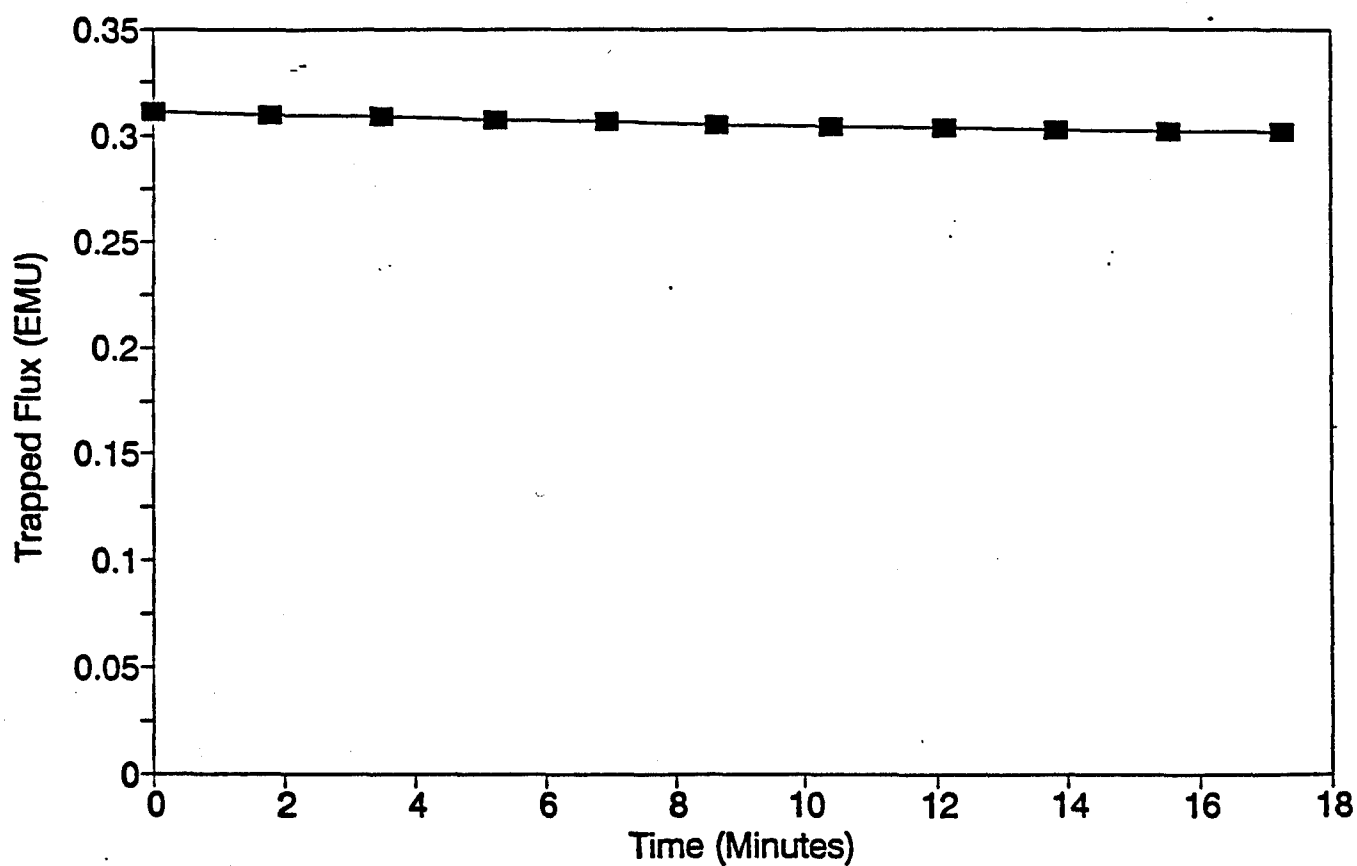
(T=10K, H=1000G)

Figure 7. Trapped flux vs time for Ag-coated Bi2212 thick-film Ag-foil sandwich. Sample 7/2/93A. T=10K. H=1,000G.

14

Trapped Flux vs Applied Field
Ag-coated Bi2212 sample 7/2/93A
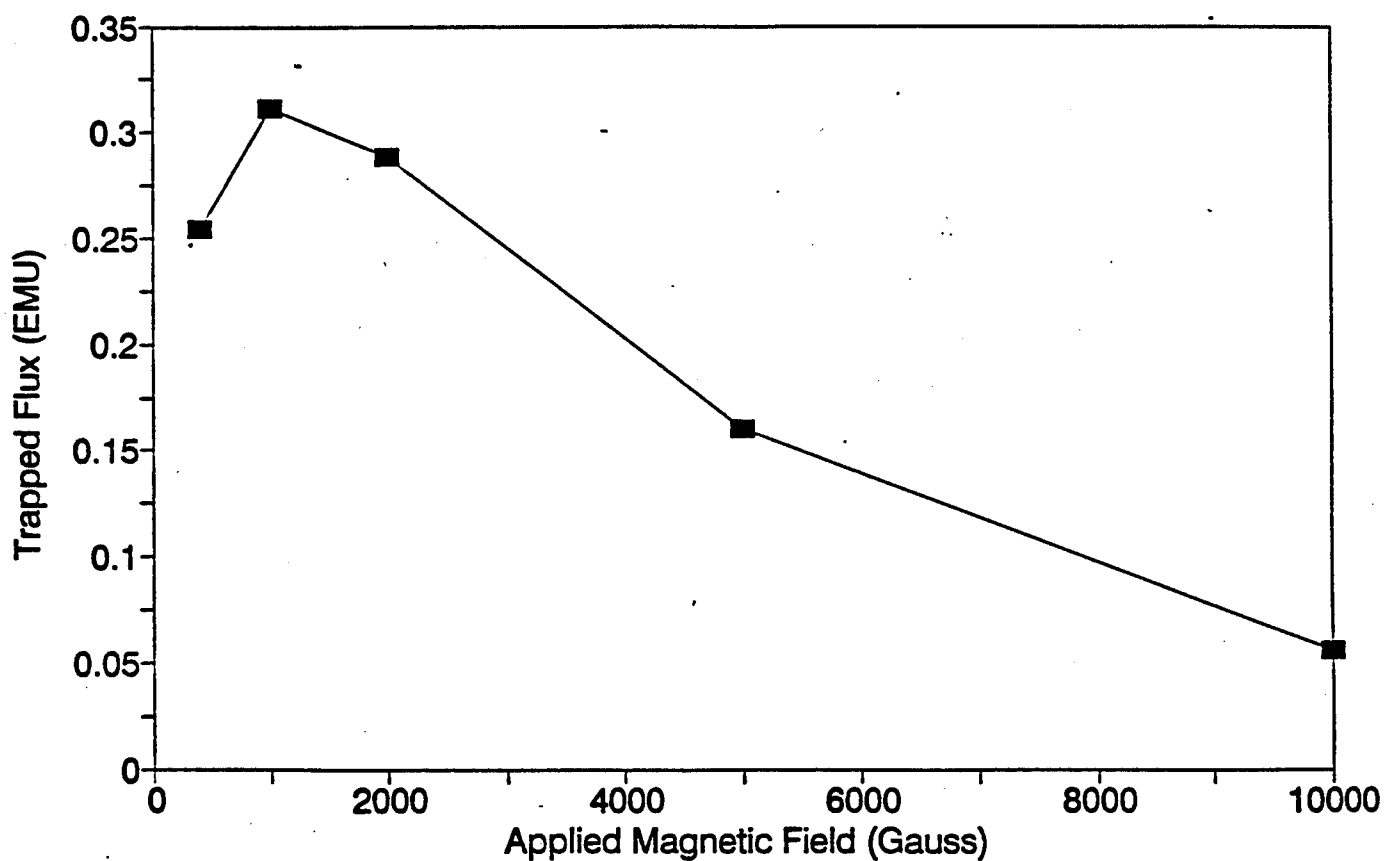
(T=10K)

Figure 8.   Trapped flux vs applied magnetic field for Ag-coated
Bi2212 thick-film Ag-foil sandwich. Sample 7/2/93A.
T=10K.

Ag-COATED BiPb2223 Hi-Tc SUPERCONDUCTORS

For $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_x$, Ag-coating did not degenerate Tc of the powder as revealed by magnetic susceptibility measurements.

For Ag-coated BiPb2223, thick-film, Ag-foil, sandwich-magnets, the optimum processing/annealing temperature is extremely critical. For uncoated BiPb2223 powders, the optimum processing/annealing temperature was 845C, but this is too hot for the Ag-coated powder since it lowers Tc below 108K. A processing/annealing temperature of 840C maintains Tc at 108K. The critical current for our best Ag-coated BiPb2223 thick-film sandwich (sample 8/4/93A) (Figure 9) is ~-29% lower than the uncoated material. Thus, we did not obtain any improvement in Jc with Ag-coating. Again, the trapped flux peaked ~1,000G which limits performance to this range.

For BiPb2223 Ag-foil constructions, a wide range of Ag-film-thicknesses and sintering temperatures were examined (Table 4) for two different particle sizes (~3um and ~15um) and measured (Table 5) with no improvement in Jc as shown in Figure 10. Clearly the larger particle size (~15um) gives superior performance in these experiments. From the literature, it is clear that related techniques of adding Ag powder to the Hi-Tc powder before fabrication greatly increases ductility and strain tolerance which is very beneficial for SuperconiX wire/tape projects.

16

Jc vs H
BiPb2223 (T=10K)
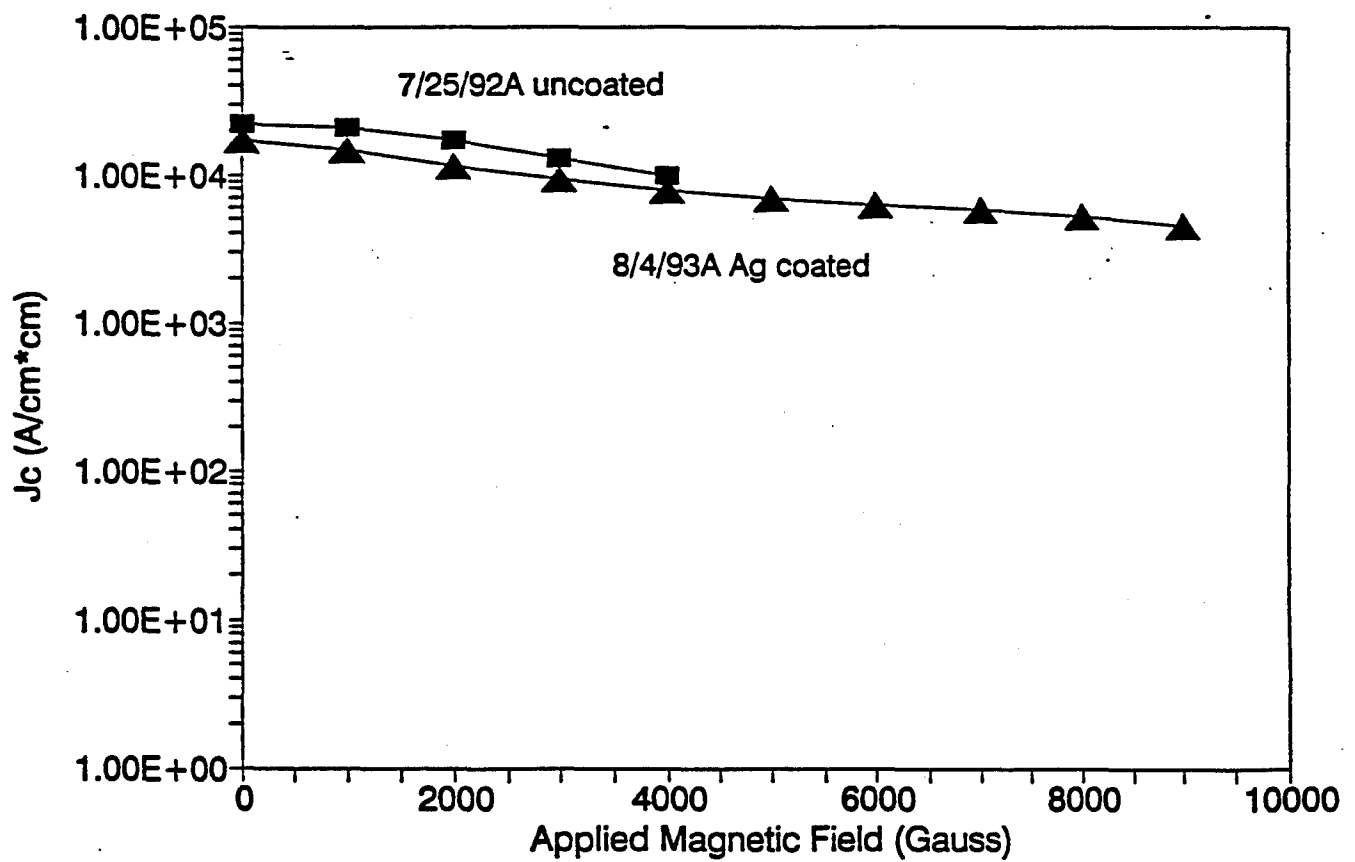
Figure 9. Critical current density (Jc) vs magnetic field for uncoated and Ag-coated BiPb2223 thick-film Ag-foil sandwich. Uncoated sample 7/25/92A. Ag-coated sample 8/4/93A. T=10K.

17

Jc vs H
Sample 9/1/93ABC & 8/11/93ABC BiPb2223
T=10K

Solid markers Particle size = (2-4um)
Hollow markers Particle size = (15um)

Legend:
- Ag=.14u
- Ag=.28u
- Ag=.35u
- Ag=.86u
- Ag=2.24u
- Ag=2.6u

Y-axis: Jc (A/cm*cm), values 0.00E+00, 2.00E+03, 4.00E+03, 6.00E+03, 8.00E+03, 1.00E+04, 1.20E+04

X-axis: H (Gauss), values 0, 2000, 4000, 6000, 8000, 10000
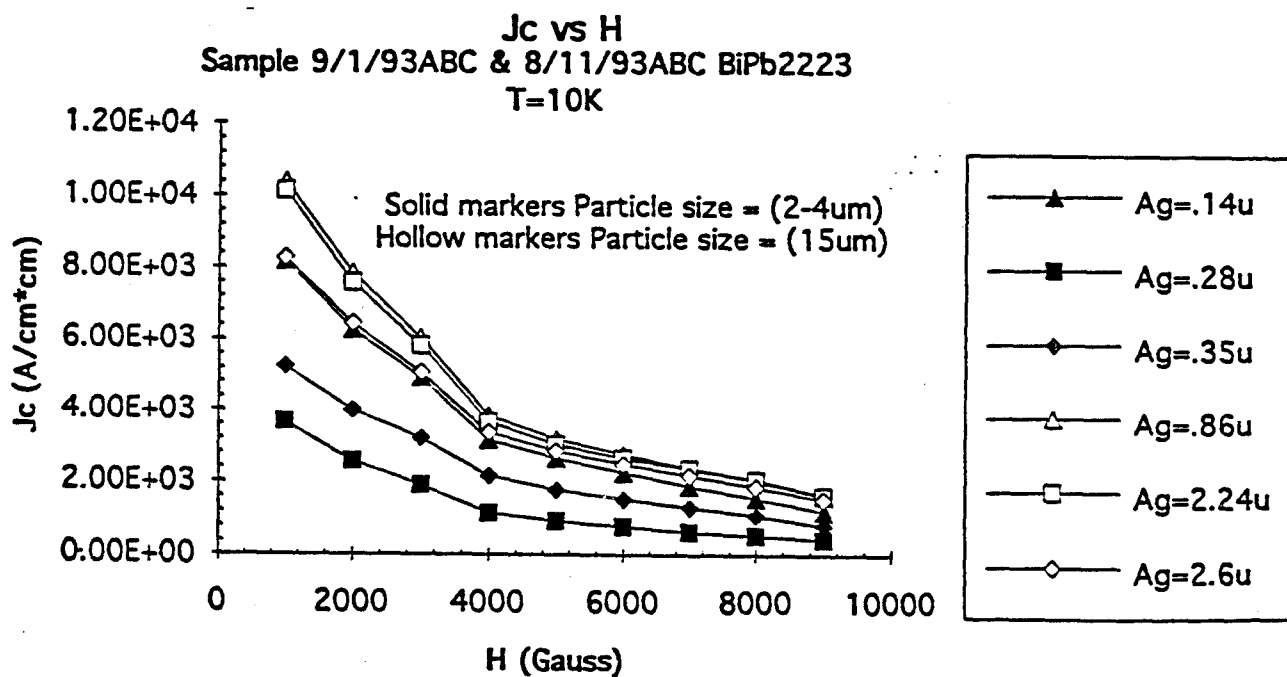
Figure 10. Critical current density (Jc) vs magnetic field for various thicknesses of Ag-coated BiPb2223 powder of two different particle sizes (~3um & 15um) fabricated into thick-film Ag-foil sandwiches. T=10K.

18

LOW Tc - COATED BiPb2223 Hi-Tc SUPERCONDUCTORS

Since Ag-coating the BiPb2223 powder only led to comparable Jc, emphasis was switched to metal-coatings (Nb, Pb, NbN) that are themselves superconducting at low temperatures. The conceived improvement follows. The Hi-Tc cuprate superconductors have very short coherence lengths ~10A-20A which causes detrimental weak-link problems at the grain boundaries. However, classical metal superconductors (Nb, Pb, NbN) have very long coherence lengths ~2,000A. Thus, if the Hi-Tc grain boundaries are filled with Low Tc metals, strong superconducting links should be created at low temperatures. At the higher temperatures, proximity-effect super-conductivity may be introduced into the metallic grain boundaries by the Hi-Tc superconductors.

Nb-COATED BiPb2223 Hi-Tc SUPERCONDUCTORS

The BiPb2223 Hi-Tc powders that were Nb-coated by cathodic arc deposition are described in Table 1. The Nb-coating processes did NOT degrade the BiPb2223 powder as revealed by magnetic susceptibility measurements of the superconducting transition temperature (Tc) of the powders (Table 2). However, only sporadic evidence (Tables 3 & 5) of superconducting Nb (Tc=9.2K) was observed but usually ~4.5K (not 9.2K as expected). This is con-sistent with the fact that the Tc of superconducting Nb films varies with the substrate conditions which are rough and uncon-trolled in our case. The use a voltage-bias during cathodic-arc sputtering gave inconclusive Nb-Tc results.

From the Nb-coated BiPb2223 powders, pressed/sintered thick-film Ag-foil-sandwiches have been made (Table 4) and measured (Table 5). These Nb-coated sandwiches (Table 4) were annealed in various oxygen partial pressures (1%, 10%, 20%). Annealing in air (~20% O_2) gave the best results. Although 10% O_2 was not much worse, 1% O_2 was terrible.

For some Nb-coated BiPb2223 pressed/sintered thick-film Ag-foil-sandwiches, the Tc data clearly shows the desired BiPb2223 Tc at 108K and an additional Nb Tc at ~9K (Fig 11). Overall, however, the Nb Tc is not well controlled or reproduced.

From magnetic hysteresis data (Table 5) on the Nb-coated, pressed/sintered, thick-film, Ag-foil-sandwiches (Table 4), the critical current density (Jc) was calculated from the Bean model via Eq 1. For a sample of BiPb2223, Jc is shown in Figure 12 at 5K, 10K and 40K. Although improvements in Jc (Fig 12) and trapped flux (Fig 13) were obtained at 5K where the Nb is also superconducting, the results are not spectacular as desired. The trapped flux measurements peak at ~1,000G which limits the magnet performance. Even when superconducting, Nb did not spectacularly improve Jc or trapped flux.

Ag+Nb-COATED BiPb2223 Hi-Tc SUPERCONDUCTORS

In Tables 1-5, experiments were made by coating BiPb2223 powder with a combination of silver (Ag) then Niobium (Nb). The results were very similar to those of Nb alone as described above.

Susceptibility vs Temperature
Nb-coated=.25um BiPb2223 H=20G 10/1/93A
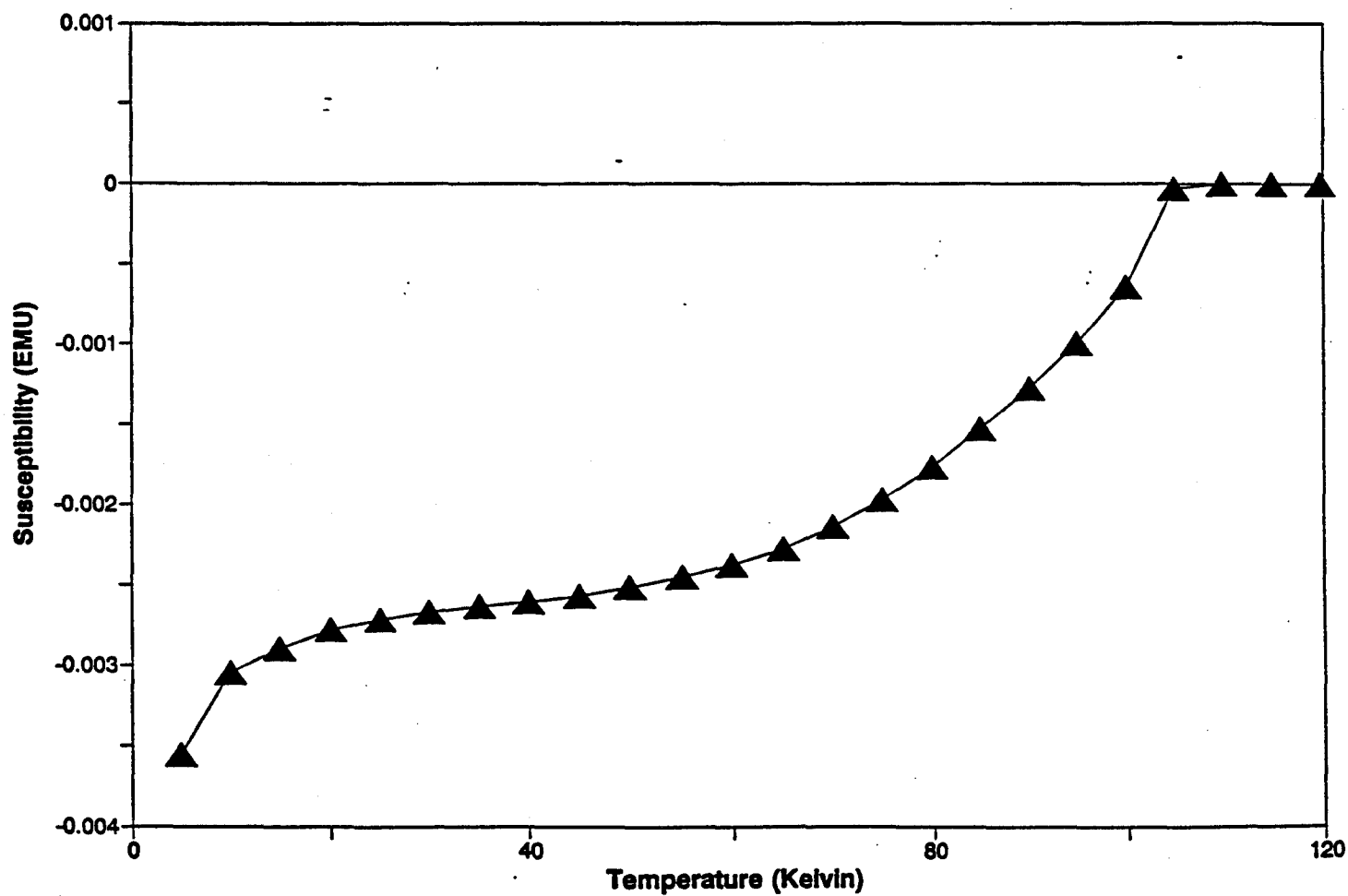
Figure 11. Magnetic susceptibility vs temperature for Nb-coated
BiPb2223 thick-film Ag-foil sandwich. Sample
10/1/93A. Note the BiPb2223 Tc=108K and the
Nb Tc=~9K.

Jc vs H
Nb-coated=.25um BiPb2223, 10/1/93A
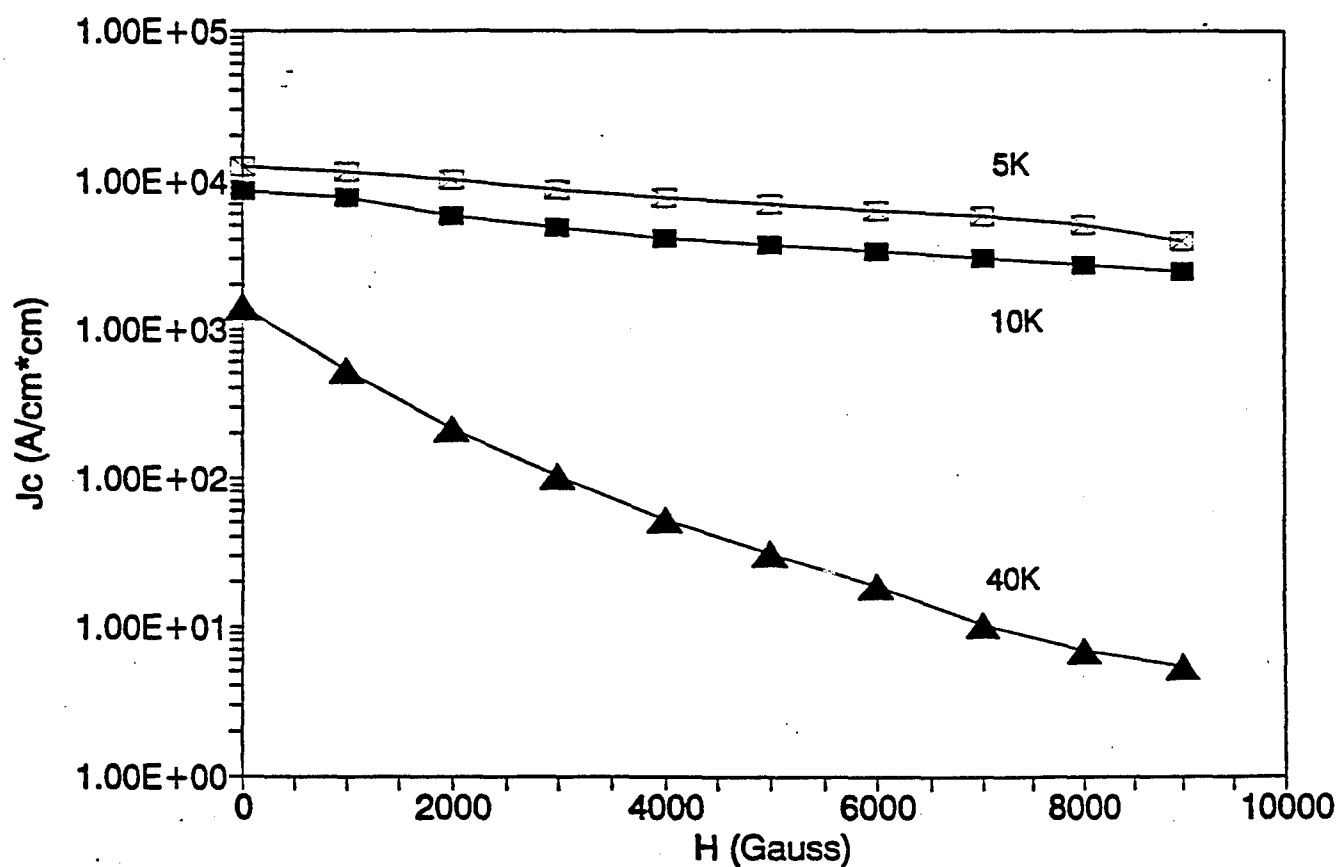
Figure 12. Critical current density (Jc) vs magnetic field for Nb-coated BiPb2223 thick-film Ag-foil sandwich. Sample 10/1/93A. T = 5K, 10K, & 40K.

Trapped Flux vs Applied Field
Nb-coated=.25um BiPb2223, 10/1/93A
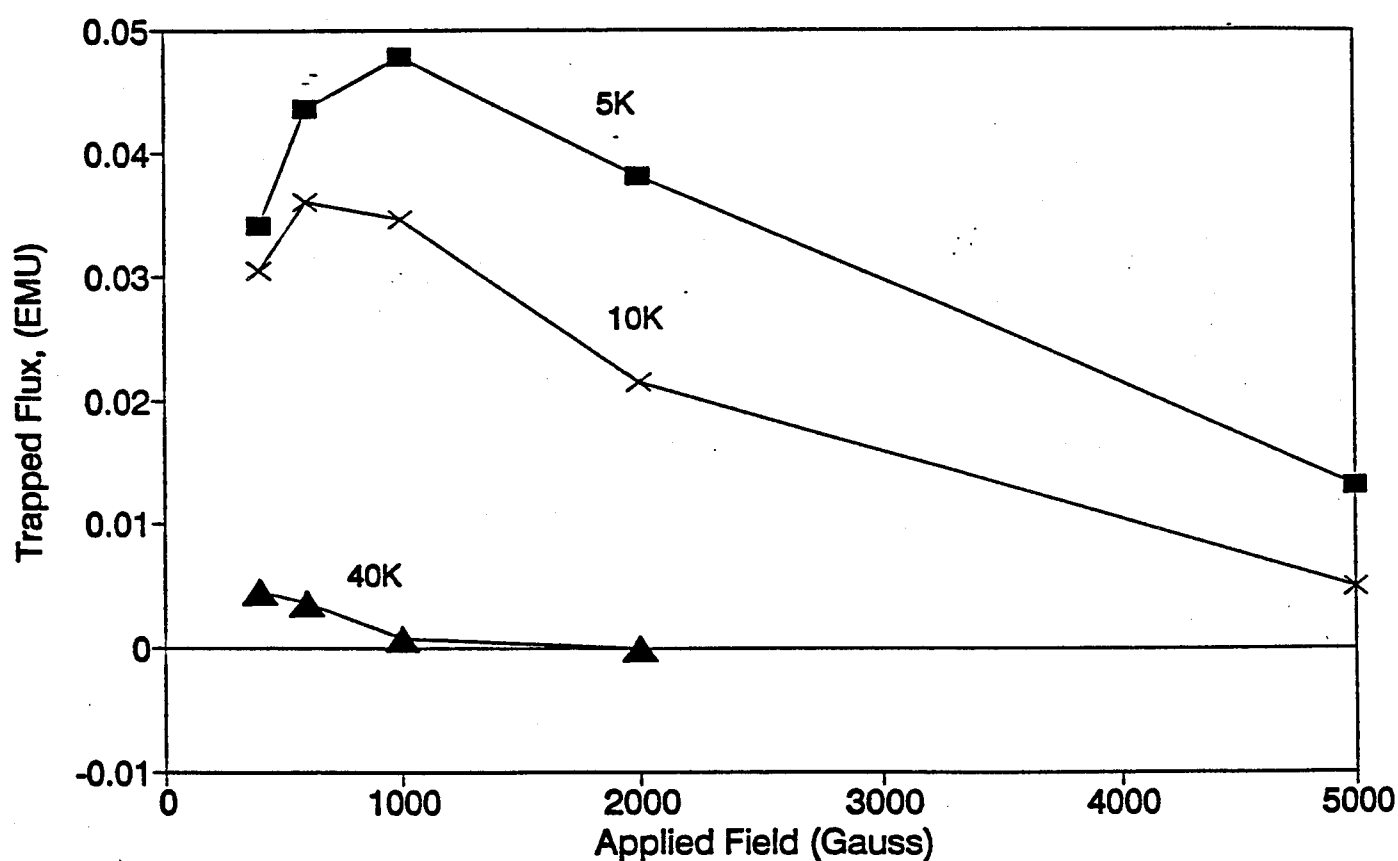
Figure 13. Trapped flux vs applied magnetic field for Nb-coated BiPb2223 thick-film Ag-foil sandwich. Sample 10/1/93A. T = 5K, 10K & 40K.

Pb-COATED BiPb2223 Hi-Tc SUPERCONDUCTORS

The Hi-Tc Pb-coated powders, magnet-sandwich constructions, and their measurements are described in Table 1, 2, 4 & 5.

Under some sputtering conditions, the Pb-coating process chemically degraded the BiPb2223 powder (Tc=108K) to the Bi2212 (Tc~80K) phase as evidenced from Tc magnetic susceptibility measurements (Table 2). However, with low sputtering power for Pb-coating, Tc=108K was maintained while the Pb superconductivity was dramatically evidenced at 7.2K in Figure 14. These low-power Pb results on powders appeared promising.

When Pb-coated BiPb2223 (Tc=108K) superconducting powder was sintered at sufficiently high temperatures to form sturdy Hi-Jc Ag-foil, thick-film sandwiches, chemical transformation (degradtion) to the Bi2212 (Tc=80K) phase occurred under all other variables including Pb thickness and particle size (3um & 15um). As shown in Figure 15, no improvements in Jc or trapped flux were obtained even at 5K where our Pb is erratically superconducting (Tc=7.2K).

NbN Lo-Tc SUPERCONDUCTOR

Attempts were made to produce Nb_xN_y superconductor (Tc = 6K to 16K) by sputtering (from a Nb powder target) and by cathodic arc deposition (from a solid Nb target). Preliminary results (Table 3) on substrates (glass & aluminum) gave some superconducting Tc's = ~5K, but insufficient time prevented further pursuit.

Susceptibility of BiPb2223 Powders
Pb-coated(9/24/93B), Uncoated(9/24/93A)
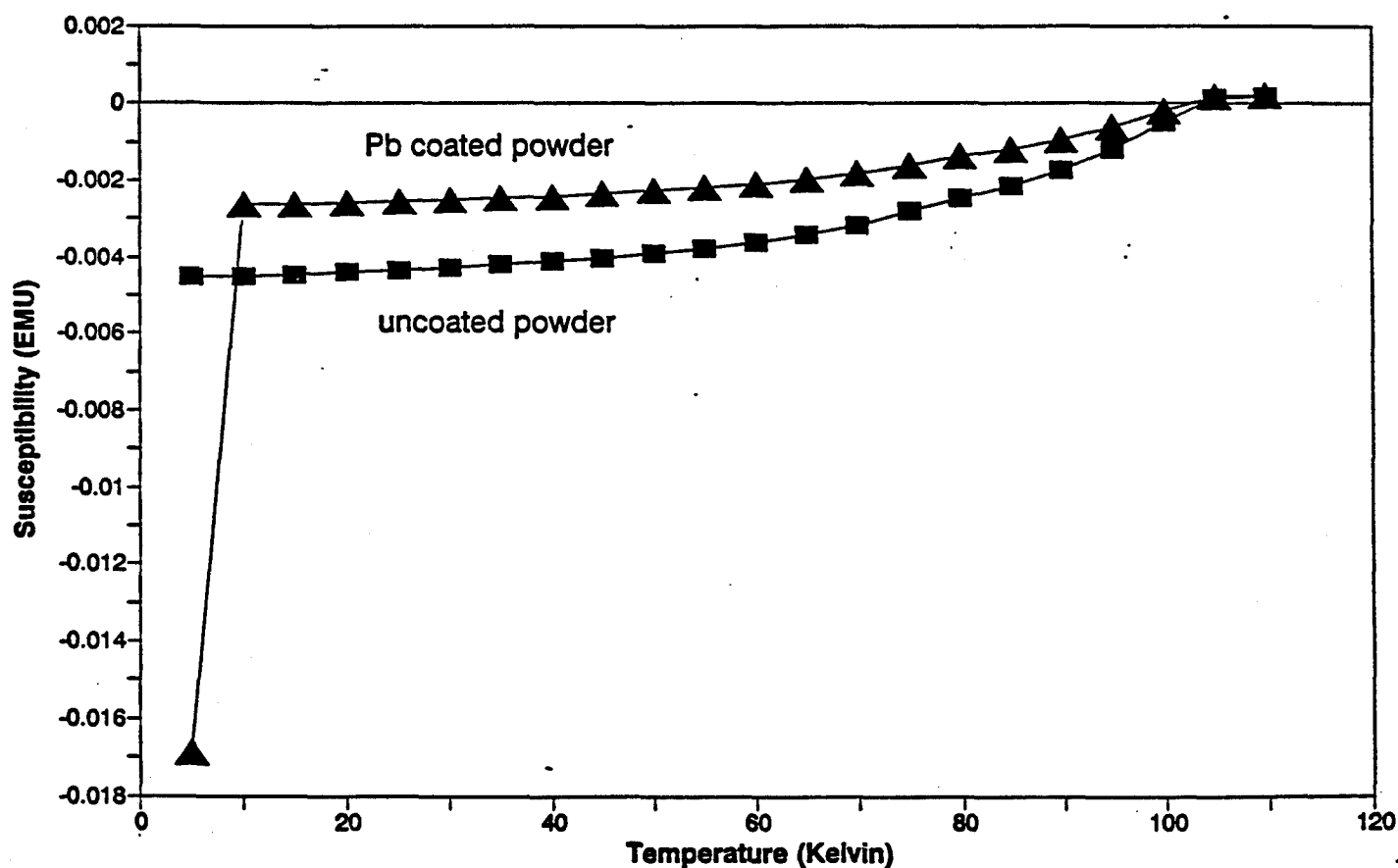
Figure 14. Magnetic susceptibility vs temperature for uncoated and Pb-coated BiPb2223 powder. Uncoated sample 9/24/93A. Pb-Coated Sample 9/24/93B. Note the BiPb2223 Tc=108K and the Pb Tc=~7K.

25

Jc vs H
Pb-coated=.0247um BiPb2223, 9/13/93B
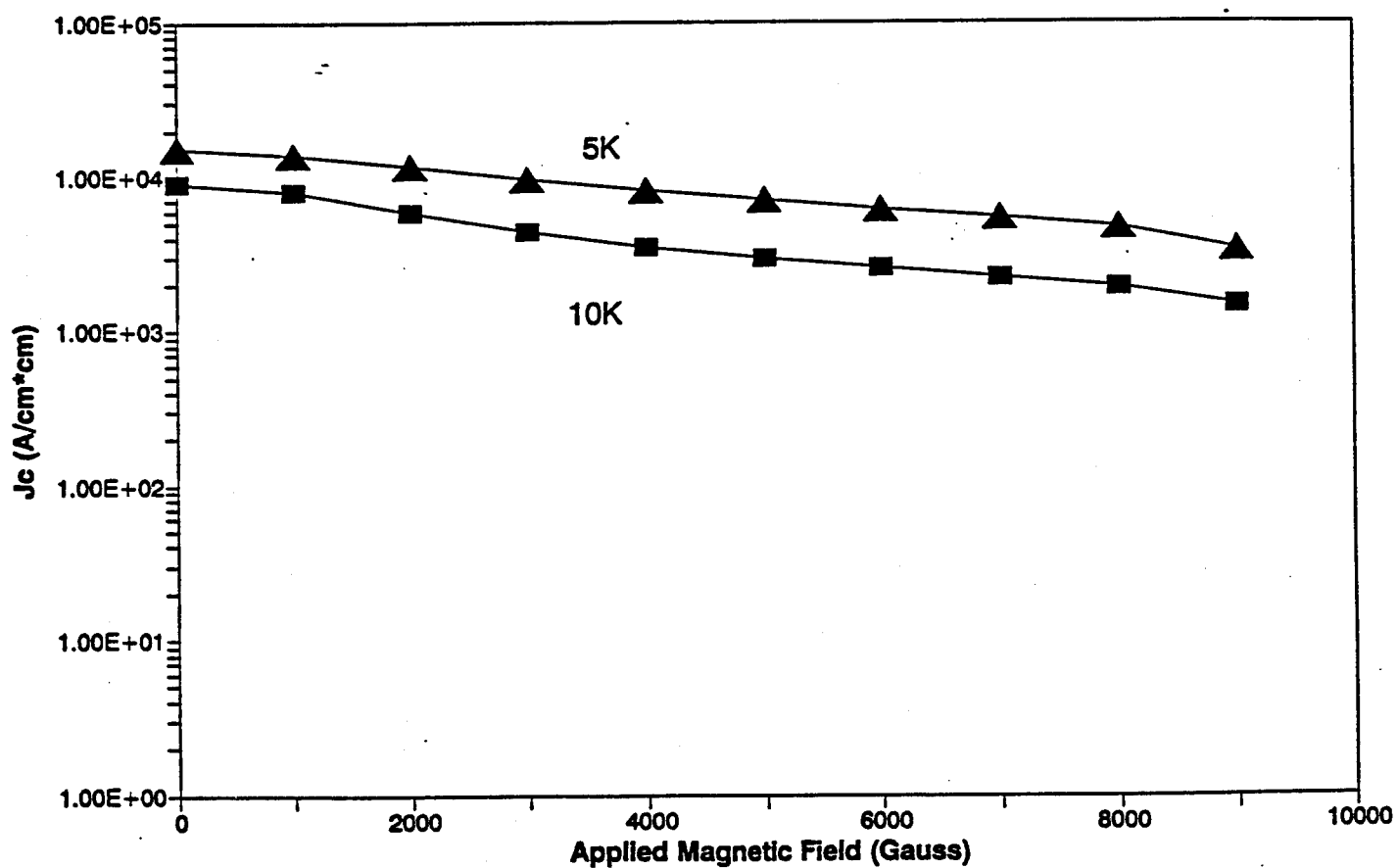
Figure 15. Critical current density (Jc) vs magnetic field for Pb-coated BiPb2223 thick-film Ag-foil sandwich. Sample 9/13/93B. T=5K & 10K.

CONCLUSIONS/RECOMMENDATIONS

The overall objective was to produce pre-formed thick-film Hi-Tc superconducting magnets with improved critical current for magnetic refrigerators. To achieve this objective, the Hi-Tc superconducting powder was coated with a thin film of beneficial metal(s) (Ag, Pb, Nb) before fabrication into pre-formed thick-film magnets. The anticipated metallic bonding between the Hi-Tc superconducting grains did NOT dramatically overcome the usual "weak-links" that limit the superconducting current. Even Lead and Niobium, which are superconducting with long coherence lengths at low temperatures, did NOT yield improvements. More specifically, regarding improvements in Jc of $Bi_2Sr_2CaCu_2O_x$ thick films, Ag-coating gave improvements of ~+131%. However, for $Bi_{1.8}Pb_{.4}Sr_2Ca_2Cu_3O_x$ thick-films, Ag-coating decreased Jc ~-29%, Nb-coating decreased Jc ~-48%, Ag+Nb-coating decreased Jc ~52%, and Pb-coating chemically deteriorated the BiPb2223 superconductor. The improvements in Jc are too marginal for further pursuit in a Phase 2 project at this time, but further efforts with other materials is justified on an exploratory basis in future Phase 1 efforts.

The Ag-coating undoubtedly improved the ductility and strain tolerance of the magnet fabrications and will be useful in another SuperconiX/Plastronics Hi-Tc superconducting wire fabrication project (NSF/SBIR Phase 2 sub-contract).

Finally, SuperconiX just completed another SDIO/SBIR contract on the use of Hi-Tc superconductors as the "magneto-caloric" medium in magnetic refrigerators (instead of the usual para/ferromagnetic materials). Very high (~100%) magneto-caloric temperature ratios have been obtained at low temperatures (<10K) which may extend the useful range of magnetic refrigerators. However, efficient refrigerator operation at higher temperatures (>20K) appear untenable.

Table 1. Tabular description of Hi-Tc superconducting powders coated with thin film of different metals (Ag, Nb, Pb).

COATING CODE	Hi-Tc POWDER	MANUFACTURER	PARTICLE SIZE	COATING MATERIAL	COATING THICKNESS
B062293A	Y123	SSC	2-6um	Ag	
B062993A	Y123	SSC	2-6um	Ag	
B063093A	Bi2212	Celanese	20um	Ag	
B071993A	BiPb2223	Celanese	15um	Ag	2.24u
B081193A	BiPb2223	Celanese	15um	Ag	.86u
B081193B	BiPb2223	Celanese	15um	Ag	2.60u
B083193A	BiPb2223	Celanese	2-4um	Ag	.14u
B083193B	BiPb2223	Celanese	2-4um	Ag	.28u
B083193C	BiPb2223	Celanese	2-4um	Ag	.35u
B091393B	BiPb2223	Celanese	15um	Pb	.0247u
B091393C	BiPb2223	Celanese	15um	Pb	.0486u
B091393D	BiPb2223	Celanese	15um	Pb	.0670u
B091493A	BiPb2223	Celanese	2-4um	Pb	.3274u
B091593A	BiPb2223	Celanese	2-4um	Pb	.4015u
B091593B	BiPb2223	Celanese	2-4um	Pb	.5003u
B092393A	BiPb2223	Celanese	2-4um	Pb(Lo-P)	.0315u
B093093BC	BiPb2223	Celanese	15um	Nb	.25u
B100693A	BiPb2223	Celanese	15um	Nb	.4166u
B100693B	BiPb2223	Celanese	15um	Nb	.5833u
B101493B	BiPb2223	Celanese	15um	Nb (300V)	.20u
B102193A	BiPb2223	Celanese	15um	Ag	.28u
				Nb (300V)	.30u

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

Table 2. Tabular description of measurements on Hi-Tc
superconducting powders (coated & uncoated).

SAMPLE CODE	MANUFACTURER. PARTICLE SIZE	COATING CODE	COATING/ THICKNESS.	FORM	MEASUREMENT
8/3/93B BiPb2223	Celanese 15um	None	Uncoated	Powder 15um	Tc=108K
8/3/93A BiPb2223	Celanese 15um	B071993A	Ag=2.24u	Powder 15um	Tc=108K
9/21/93A BiPb2223	Celanese 2-4um	B091593B	Pb=.5003u	Powder 2-4um	Tc=88K
9/24/93A BiPb2223	Celanese 2-4um	None	Uncoated	Powder 2-4um	Tc=105K
9/24/93B BiPb2223	Celanese 2-4um	B092393A	Pb=.0315u (low power)	Powder 2-4um	Tc=105K
9/30/93A BiPb2223	Celanese 15um	B093093BC	Nb=.25u	Powder 15um	Tc=108K
10/06/93B BiPb2223	Celanese 15um	B100693B	Nb=.5833u	Powder 15um	Tc=108K
10/14/93B BiPb2223	Celanese 15um	B101493B	Nb=.20u Bias 300V	Powder 15um	Tc=108K
10/21/93A BiPb2223	Celanese 15um	B102193A	Ag=.28u Nb=.30u Bias 300V	Powder 15um	Tc=105k

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

Table 3. Tabular description of measurements on substrates coated with superconducting (Nb & NbN) films.

COATING CODE	COATING/ THICKNESS.	SUBSTRATE/ DESCRIPTION	MEASUREMENT
B-100693-A&B	Nb=.58um	glass	Tc=0 K
B-101493-B +B-102093-A	Nb=.60um	glass	Tc=4K
B-102193-A	Ag=.28um Nb=.30um	glass	Tc=4.5K
B-102893-A	NbN_x N_2=25mTorr	glass	Tc=0 K
B-102893-B	NbN_x N_2=4mTorr	glass	Tc=4.5K
B-102893-XA	NbN_x N2 cumulative.	Al foil. Dark blue, shiny.	Tc=0 K
B-102893-XB	NbN_x N2 cumulative.	Al foil. Dark blue, dull.	Tc=5K
B-111593-B	NbN_x N2=3mTorr Ar=7mTorr	glass. yellow-green	Tc=0K

Table 4. Tabular description of the preparation of Hi-Tc superconducting thick-film Ag-foil sandwich samples (thick-film pre-formed magnets).

SAMPLE CODE	MANUFACTURER PARTICLE SIZE	COATING CODE	COATING MATERIAL/ THICKNESS	MAX TEMP (C)	ANNEAL TEMP (C)	ANNEAL GAS
7/2/93 Bi2212	Celanese 20um	B063093A	Ag	895	860	$100\%O_2$ $10\% \ O_2$
7/13/93 Bi2212	Celanese 20um	B063093A	Ag	890	860	$10\% \ O_2$
7/26/93 BiPb2223	Celanese 15um	B071993A Ag=2.24u	Ag=2.24u	845	845	$1\% \ O_2$ Air
7/30/93 BiPb2223	Celanese 15um	B071993A Ag=2.24u	Ag=2.24u	?845	?845 New furnace	$10\% \ O_2$ too hot.
8/4/93A BiPb2223	Celanese 15um	B071993A Ag=2.24u	Ag=2.24u	840	840	$10\% \ O_2$
8/11/93B BiPb2223	Celanese 15um	B071993A Ag=2.24u	Ag=2.24u	842.5	842.5	$10\% \ O_2$
8/11/93A BiPb2223	Celanese 15um	B081193A Ag=.86u	Ag=.86u	842.5	842.5	$10\% \ O_2$
8/11/93C BiPb2223	Celanese 15um	B081193B Ag=2.6u	Ag=2.6u	842.5	842.5	$10\% \ O_2$
9/1/93A BiPb2223	Celanese 2-4um	B083193A Ag=.14u	Ag=.14u	842.5	842.5	$10\% \ O_2$
9/1/93B BiPb2223	Celanese 2-4um	B083193B Ag=.28u	Ag=.28u	842.5	842.5	$10\% \ O_2$
9/1/93C BiPb2223	Celanese 2-4um	B083193C Ag=.35u	Ag=.35u	842.5	842.5	$10\% \ O_2$
9/7/93A BiPb2223	Celanese 2-4um	B083193A Ag=.14	Ag=.14u	835	835	$10\% \ O_2$
9/7/93B BiPb2223	Celanese 2-4um	B083193B Ag=.28	Ag=.28u	835	835	$10\% \ O_2$
9/7/93C BiPb2223	Celanese 2-4um	B083193C Ag=.35	Ag=.35u	835	835	$10\% \ O_2$

Table 4. Continued.

SAMPLE CODE	MANUFACTURER PARTICLE SIZE	COATING CODE	COATING MATERIAL/ THICKNESS	MAX TEMP (C)	ANNEAL TEMP (C)	ANNEAL GAS
9/13/93B BiPb223	Celanese 15um	B091393B Pb=.0247u	Pb=.0247u	825	825	$10\%O_2$
9/13/93C BiPb2223	Celanese 15um	B091393C Pb=.0486u	Pb=.0486u	825	825	$10\%O_2$
9/13/93D BiPb2223	Celanese 15um	B091393D Pb=.0670u	Pb=.0670u	825	825	
9/17/93A BiPb2223	Celanese 2-4um	B091493A Pb=.3274u	Pb=.3274u	832	832	$10\%O_2$
9/17/93B BiPb2223	Celanese 2-4um	B091593A Pb=.4015u	Pb=.4015u	832	832	$10\%O_2$
9/17/93C BiPb2223	Celanese 2-4um	B091593B Pb=.5003u	Pb=.5003u	832	832	$10\%O_2$
9/22/93A BiPb2223	Celanese 2-4um	B091493A Pb=.3274u	Pb=.3274u	500	500	$10\%O_2$
9/22/93B BiPb2223	Celanese 2-4um	B091493A Pb=.3274u	Pb=.3274u	650	650	$10\%O_2$
9/22/93C BiPb2223	Celanese 2-4um	B091493A Pb=.3274u	Pb=.3274u	800	800	$10\%O_2$
9/29/93A BiPb2223	Celanese 2-4um	B092393A Pb=.0315u	Pb=.0315u	825	825	$10\%O_2$

32

Table 4. Concluded.

SAMPLE CODE	MANUFACTURER PARTICLE SIZE	COATING CODE	COATING MATERIAL/ THICKNESS	MAX TEMP (C)	ANNEAL TEMP (C)	ANNEAL GAS
10/1/93A BiPb2223	Celanese 15um	B093093BC Nb=.25u	Nb=.25u	840	840	$10\%O_2$
10/7/93A BiPb2223	Celanese 15um	B100693A Nb=.4166u	Nb=.4166u	840	840	$1\%O_2$
10/7/93B BiPb2223	Celanese 15um	B100693B Nb=.5833u	Nb=.5833u	840	840	$1\%O_2$
10/15/93A BiPb2223	Celanese 15um	B101493B Nb=.20u	Nb=.20u (300V)	840	840	$1\%O_2$
10/22/93A BiPb2223	Celanese 15um	B102193A Ag=.28u Nb=.30u	Ag=.28u Nb=.30u (300V)	840	840	$10\%O_2$
10/27/93Nb BiPb2223	Celanese 15um	B093093BC Nb=.25u	Nb=.25u	840	840	Air $(20\%O_2)$
10/27/93 Nb+Ag BiPb2223	Celanese 15um	B102193A Ag=.28u Nb=.30u	Ag=.28u Nb=.30u (300V)	840	840	Air $(20\%O_2)$

Table 5.   Tabular summary of measurements on Hi-Tc
          superconducting thick-film magnets. The following
          abbreviated codes are used.
M = Magnetic Moment.
T = Temperature.
t = time.
H = Magnetic Field.
Tc = Superconducting transition temperature.
ZFC = Zero field cooled.
FC = Field cooled.
FW = Field warmed.

SAMPLE   MEASUREMENTS

7/2/93   (ZFC) M vs T (FW H=20G) (H perp)   (Tc=90K)
Bi2212   M vs H Hysteresis (H perp) at T = 10K, 40K, 70K.
Celanese   FC Trapped Flux. M vs t (10K, 40K)
Ag=?   FC Trapped Flux vs Applied Magnetic Field (10K, 40K)

7/13/93   (ZFC) M vs T (FW H=20G) (H perp)   (Tc=75K)
Bi2212   M vs H Hysteresis (H perp) at T = 10K, 40K, 70K.
Celanese   FC Trapped Flux. M vs t (10K, 40K)
Ag=?   FC Trapped Flux vs Applied Magnetic Field (10K, 40K)

7/26/93A   (ZFC) M vs T (FW H=20G) (H perp)   (Tc=80K)
BiPb2223   M vs H Hysteresis (H perp) at T=10K, 40K, 70K.
Celanese   FC Trapped Flux. M vs t (10K, 40K)
Ag=2.24u   FC Trapped Flux vs Applied Magnetic Field (10K, 40K)

7/26/93B   (ZFC) M vs T (FW H=20G) (H perp)   (Tc=65K)
BiPb2223
Celanese
Ag=2.24u

7/30/93   (ZFC) M vs T (FW H=20G) (H perp)   (Tc=0 K)
BiPb2223   (New Uncontrolled Furnace Too Hot)
Celanese
Ag=2.24u

8/3/93A   (ZFC) M vs T (FW H=20G)   (Tc=108K)
BiPb2223 - Ag Coated POWDER.
Celanese - Ag=2.24u.
Ag=2.24u

8/3/93B   (ZFC) M vs T (FW H=20G)   (Tc=108K)
BiPb2223 - Uncoated POWDER.
Celanese - Uncoated POWDER.
Uncoated

8/4/93A   (ZFC) M vs T (FW H=20G) (H perp)   (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at T=10K, 40K, 70K)
Celanese   FC Trapped Flux. M vs t (10K)
Ag=2.24u   FC Trapped Flux vs Applied Magnetic Field (10K)

Table 5.   Continued.

```
8/11/93A   (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K, 70K)
Celanese   FC Trapped Flux. M vs t (10K,40K)
Ag=.86u    FC Trapped Flux vs Applied Magnetic Field (10K,40K)


8/11/93B   (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K, 70K)
Celanese   FC Trapped Flux. M vs t (10K,40K)
Ag=2.24u   FC Trapped Flux vs Applied Magnetic Field (10K,40K)


8/11/93C   (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K, 70K)
Celanese   FC Trapped Flux. M vs t (10K,40K)
Ag=2.6u    FC Trapped Flux vs Applied Magnetic Field (10K,40K)
---------------------------------------------------------------------
9/1/93A    (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K)
Celanese   FC Trapped Flux. M vs t (10K)
Ag=.14u    FC Trapped Flux vs Applied Magnetic Field (10K)


9/1/93B    (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K)
Celanese   FC Trapped Flux. M vs t (10K)
Ag=.28u    FC Trapped Flux vs Applied Magnetic Field (10K)


9/1/93C    (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K)
Celanese   FC Trapped Flux. M vs t (10K)
Ag=.35u    FC Trapped Flux vs Applied Magnetic Field (10K)
---------------------------------------------------------------------
9/7/93A    (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K, 40K)
Celanese   FC Trapped Flux. M vs t (10K, 40K)
Ag=.14u    FC Trapped Flux vs Applied Magnetic Field (10K)


XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX


9/13/93B   (ZFC) M vs T (Fw H=20G) (H perp)                    (Tc=70K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K)
Celanese   FC Trapped Flux M vs t (5K, 10K)
Pb=.0247u  FC Trapped Flux vs Applied Magnetic Field (5K, 10K)


9/13/93C   (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=75K)
BiPb2223   M vs H Hysteresis (H perp) at (T=10K)
Celanese
Pb=.0486u
---------------------------------------------------------------------
9/17/93C   (ZFC) M vs T (FW H=20G) (H perp)                    (Tc=55K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K)
Celanese
Pb=.5003u
---------------------------------------------------------------------
```

Table 5. Continued.

```
9/21/93A   (ZFC) M vs T (FW H=20G)                        (Tc=88K)
BiPb2223   -Pb Coated POWDER
Celanese   -Pb = .5003um
Pb=.5003u
------------------------------------------------------------------
9/22/93C   (ZFC) M vs T (FW H=20G)                        (Tc=60K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K, 40K)
Celanese   FC Trapped Flux. M vs t (5K, 10K, 40K)
Pb=.3274u FC Trapped Flux vs Applied Magnetic Field (5k,10K,40K)
------------------------------------------------------------------
9/24/93A   (ZFC) M vs T (FW H=20G)                        (Tc=105K)
BiPb2223   -Uncoated POWDER
Celanese   -Uncoated POWDER
Uncoated

9/24/93B   (ZFC) M vs T (FW H=20G)                        (Tc=105K)
BiPb2223   -Pb coated POWDER
Celanese   -Pb = .0315um
Pb=.0315u
------------------------------------------------------------------
9/29/93A   (ZFC) M vs T (FW H=20G)                        (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K)
Celanese
Pb=.0315u


XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

9/30/93A   (ZFC) M vs T (FW H=20G)                        (Tc=108K)
BiPb2223   -Nb coated POWDER
Celanese   -Nb = .25um
Nb=.25u
------------------------------------------------------------------
10/1/93A   (ZFC) M vs T (FW H=20G)                        (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=2K, 5K, 10K, 40K)
Celanese   FC Trapped Flux. M vs t (5K, 10K, 40K)
Nb=.25u    FC Trapped Flux vs Applied Magnetic Field (5K,10K,40K)
------------------------------------------------------------------
10/6/93B   (ZFC) M vs T (FW H=20G)                        (Tc=108K)
BiPb2223   -Nb coated POWDER
Celanese   -Nb = .5833um
Nb=.5833u
------------------------------------------------------------------
10/7/93A   (ZFC) M vs T (FW H=20G)                        (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K)
Celanese   FC Trapped Flux. M vs t (5K, 10K)
Nb=.4166u FC Trapped Flux vs Applied Magnetic Field (5K, 10K)

10/7/93B   (ZFC) M vs T (FW H=20G)                        (Tc=105K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K)
Celanese   FC Trapped Flux. M vs t (5K, 10K)
Nb=.5833u FC Trapped Flux vs Applied Magnetic Field (5K, 10K)
------------------------------------------------------------------
```

Table 5. Concluded.

```
10/14/93B  (ZFC) M vs T (FW H=20G)                              (Tc=108K)
BiPb2223   -Nb coated POWDER
Celanese   -Nb = .20um
Nb=.20u
```

```
10/15/93A  (ZFC) M vs T (FW H=20G)                              (Tc=108K)
BiPb2223   M vs H Hysteresis (H perp) at (T=5K, 10K)
Celanese   FC Trapped Flux. M vs t (5K, 10K)
Nb=.20u    FC Trapped Flux vs Applied Magnetic Field (5K, 10K)
300V bias
```

```
10/27/93Nb (ZFC) M vs T (FW H=20G)                         .    (Tc=105K)
BiPb2223   M vs H Hysteresis (H perp) at (T=2K, 5K, 10K)
Celanese   FC Trapped Flux. M vs t (2K, 5K)
Nb=.25u    FC Trapped Flus vs Applied Magnetic Field (2K, 5K)
```

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

```
10/21/93A  (ZFC) M vs T (FW H=20G)                              (Tc=105K)
BiPb2223   Ag, Nb coated POWDER
Celanese
Ag = .28um
Nb = .30um(300V bias)
```

```
10/22/93A  (ZFC) M vs T (FW H=20G)                              (Tc=105K)
BiPb2223   M vs H Hysteresis (H perp) at (T=2K, 5K, 10K)
Celanese   FC Trapped Flux. M vs t (2K, 5K)
Ag=.28um   FC Trapped Flux vs Applied Magnetic Field (2K, 5K)
Nb=.30um(300V bias)
```

```
10/27/93   (ZFC) M vs T (FW H=20G)                              (Tc=105K)
BiPb2223   M vs H Hysteresis (H perp) at (T=2K, 5K, 10K)
Celanese   FC Trapped Flux. M vs t (2K, 5K, 10K)
Ag=.28um   FC Trapped Flux vs Applied Magnetic Field (2K)
Nb=.30um(300v bias).
```

37

DISTRIBUTION LIST

AUL/LSE
Bldg 1405 - 600 Chennault Circle
Maxwell AFB, AL 36112-6424   1 cy

DTIC/OCP
8725 John J. Kingman Rd Ste 944
FT Belvoir, VA 22060-6218   2 cys

AFSAA/SAI
1580 Air Force Pentagon
Washington, DC 20330-1580   1 cy

PL/SUL
Kirtland AFB, NM 87117-5776   2 cys

PL/HO
Kirtland AFB, NM 87117-5776   1 cy

Official Record Copy

PL/VTP/Marko Stoyanof   2 cys

Dr. R. V. Wick   1 cy
PL/VT
Kirtland, AFB, NM 87117-5776